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CELEBRATING THE 350TH ANNIVERSARY OF DISCOVERING PHOSPHORUS—FOR BETTER OR WORSE

Direct Exports of Phosphorus from Fertilizers Applied to Grazed Pastures

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Abstract

Since its discovery in 1669, phosphorus (P) in the form of fertilizer has become an essential input for many agroecosystems. By introducing a concentrated P source, fertilizers increase short-term P export potential soon after their application and longer-term export potential by increasing soil fertility (legacy P). The 4R concept was developed to help mitigate P exports from the fertilizers that sustain agricultural productivity. This review investigates the factors affecting P exports soon after the application of mineral fertilizers to pasture-based grazing systems and studies quantifying its potential impact in different systems, with an emphasis on Australasia. Initially, P fertilizers and reactions that might affect their short-term P export potential are reviewed, along with P transport pathways, the forms of P exported from grazing systems, factors affecting P mobilization into water, and studies demonstrating the possible short-term effects of fertilizer application on P exports. Using that foundation, we review studies quantifying the short-term impact of fertilizer application in different regions; they show that under poor management, recently applied fertilizer can contribute a considerable proportion (30–80%) of total farm P exports in drainage, but when fertilizer is well-managed, that figure is expected to be <10%. We then use three model systems of varying hydrology that are common to Australasia to demonstrate the principles for selecting fertilizers that are likely to minimize P exports soon after their application.

Core Ideas

- Fertilizers increase P exports directly or by increasing P cycling.
- We review P pathways and processes relevant to grazing systems.
- Direct fertilizer P exports can be comparatively small (<10% of annual exports).
- Fertilizer selection to minimize P exports in three model systems is demonstrated.

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Phosphorus (P) is the sixth most abundant element in living organisms. Since its discovery in 1669, P has become an essential input for many agroecosystems (Lun et al., 2018; Sharpley et al., 2018), and P amendments have facilitated our transition to modern urbanized societies. However, the use of P amendments in agriculture has not been without its challenges. The application of amendments and accumulation of P in agricultural soils (Stutter et al., 2015; Tian et al., 2017) have increased the risk of P in drainage adversely affecting downstream water resources (ANZECC and ARMCANZ, 2000; Brogan et al., 2001; Cooke et al., 1993; Dodds and Smith, 2016; European Environment Agency, 1998; USEPA, 1996).

In both terrestrial and aquatic systems, organisms extract P in the form of orthophosphate anions ($H_2PO_4^-$/HPO_4^{2-}) from water. The total P (TP) concentration needed in soil water for optimum agricultural production is often cited as >0.2 mg L^{-1} (Pierzynski et al., 2005). However, a soil water P concentration of ~0.9 mg L^{-1} was required for maximum pasture productivity in New Zealand field trials (Wheeler and Edmeades, 1995) and concentrations >>1 mg L^{-1} have been noted in Australia (Nash et al., 2007; Toifl et al., 2000; Watkins et al., 2012). For freshwater systems, TP concentrations designed to minimize the potential for adverse algal (viz. periphyton) growth are <0.009 to 0.07 mg L^{-1}, varying by region or jurisdiction (ANZECC and ARMCANZ, 2018; CCME, 2004; EPA, 2003; Miltner, 2010; Smith and Tran, 2010; Stevenson et al., 2008). Given that some P is always present in soil water, it follows that transfers from land to water (i.e., P exports) are an inevitable consequence of drainage from terrestrial systems (Haygarth et al., 2005) and streams draining agricultural catchments often suffer "impaired" water quality

In Australasia (i.e., Australia and New Zealand), intensive pasture-based grazing is often the primary land use in catchments with impaired water quality (Dairy Australia, 2019; McDowell et al., 2009a; Meat and Livestock Australia, 2017;

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Abbreviations: DAP, di-ammonium phosphate; DRP, dissolved reactive phosphorus; MAP, mono-ammonium phosphate; MCP, monocalcium phosphate; PR, phosphate rock; SSP, single superphosphate; TDP, total dissolved phosphorus; TP, total phosphorus; TSP, triple superphosphate.

PricewaterhouseCoopers, 2011; Sinclair Knight Merz, 2011). Although some aspects of water quality may be improving in New Zealand (Larned et al., 2016), P exports from pastures remain a concern (Ballantine and Davies-Colley, 2014; Julian et al., 2017; McDowell et al., 2009a). The New Zealand government has responded to concerns about water quality and use with its National Policy Statement for Freshwater Management (New Zealand Government, 2017). In Australia, both estuarine and freshwater systems suffer impaired water quality from P exports, for example, in Victoria and Western Australia (Birch, 1982; Grayson et al., 2001; Hallows, 1998; Webster et al., 2001). Again, despite remedial efforts (EPA, 1995), water quality in many cases remains a concern (Turral et al., 2017).

Phosphorus exports to water from pasture-based grazing systems can be conveniently divided into "systematic" (i.e., base or background)– and "incidental" (i.e., management)–related components (Haygarth and Jarvis, 1999). Conceptually, background exports are attributable to the production system and ambient conditions. Management decisions and critical incidents can increase P exports over and above those that would have otherwise occurred and include the application of inorganic fertilizer, spreading of manure, the timing of grazing, and grazing management that affects soil erosion.

Mineral (i.e., inorganic) fertilizers are highly concentrated sources of P that are often an integral part of pasture-based grazing systems and may contribute directly to "incidental" P exports soon after their application or indirectly, through increased P cycling (i.e., systematic exports) (McDowell, 2012). Internationally, the 4R nutrient stewardship concept has been used by the fertilizer industry to guide the development of fertilizer best or good management practices. The 4R concept is to apply the Right source of nutrients, at the Right rate, at the Right time, and in the Right place (Bruulsema, 2018; Johnston and Bruulsema, 2014). Good management practices consider the individual attributes of each farming system and attempt to optimize nutrient use efficiency and environmental sustainability, while supporting farm profitability. On well-managed farms, practices are adopted that address a range of soil, fertilizer, effluent management, and irrigation issues (Dairy Australia, 2018).

In this review, we address the factors affecting P exports directly associated with the application of mineral P fertilizers in pasture-based grazing systems, with an emphasis on Australasia. Our objective is to provide a scientific foundation that can underpin the application of the 4R principles and appropriate fertilizer selection and application strategies to specific farming systems. The discussion of legacy effects (i.e., systematic exports) is outside the scope of this paper. We initially investigate P fertilizer compounds and formulations commonly applied to pastures and reactions that might affect their short-term P export potential. Phosphorus transport pathways, the forms of P exported from grazing systems and the factors affecting P mobilization into water, are then explored. Using that foundation, studies examining the contribution of recently applied fertilizer to P exports in specific regions are examined. Finally, three model systems with varying hydrology that are common to Australasia are used to demonstrate the principles for fertilizer selection and management that are likely to minimize P exports soon after their application.

Common Phosphatic Fertilizers Applied to Pastures and Their Reactions with Soil

Some common P compounds in fertilizers and soil are presented in Table 1. Granular inorganic P fertilizers are often surface applied (i.e., broadcast onto pastures) and can be broadly classified as being (i) water soluble, (ii) partially water soluble, or (iii) sparingly soluble (Chien et al., 1989, 2011). The most common water-soluble phosphatic fertilizers are single- and triple-superphosphates, together with mono- and di-ammonium phosphates. Superphosphates are formed by the reaction of an acid with phosphate rock (PR). Where sulfuric acid is used, the resulting fertilizer is a combination of water-soluble monocalcium phosphate (MCP) and gypsum ($CaSO_4$) commonly referred to as single superphosphate (SSP). Single superphosphate is the dominant form of P applied to pastures in Australasia (McDowell et al., 2019). The gypsum in SSP affects the physical properties of the granules and provides sulfur, another essential nutrient for plants. If phosphoric acid, rather than sulfuric acid, is reacted with the PR, a more concentrated MCP fertilizer is produced (triple superphosphate, TSP). Ammonium phosphates are produced by reacting ammonia with phosphoric acid. The products formed depend on the molar ratios of reactants but are commonly mono- and di-ammonium phosphate (MAP and DAP). Ammonium phosphates are fully water soluble (Chien et al., 2011).

There are several partially water-soluble P fertilizers, and their chemical properties vary considerably (Chien and Menon, 1995a; Chien et al., 2009). Fertilizers in this group can be made by reacting anhydrous or aqueous ammonia with SSP or TSP, nitric acid with PR, or reactive PR with sulfuric acid or phosphoric acid to form partially acidulated phosphate rock fertilizers (Stephen and Condron, 1986; Yeates and Clarke, 1993). This group also includes fertilizers made by mixing water-soluble compounds, such as SSP, with sparingly soluble compounds such as PR or lime. Sparingly soluble or slow-release P fertilizers include reactive PR (Chien and Menon, 1995b), heat-treated (calcined) PR, and di-calcium phosphate formed by reacting hydrochloric

Table 1. Some common phosphate compounds in fertilizer and soil.†

Compound	Formula	Common name (acronym)	Phosphorus concentration	Water solubility
Monocalcium phosphate	$Ca(H_2PO_4)_2.H_2O$	Superphosphate (SSP/DSP/TSP)	Single, 9% Double, 18% Triple, 21%	High
Mono-ammonium phosphate	$NH_4H_2PO_4$	MAP	23%	High
Di-ammonium phosphate	$(NH_4)_2HPO_4$	DAP	20%	High
Di-calcium phosphate	$CaHPO_4$ $CaHPO_4.2H_2O$	DCP (anhydrous) DCP	Variable	Low
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	Phosphate rock (PR)	Variable	Low

† Adapted from Nash and Halliwell (1999).

acid with PR. This paper focuses mainly on the reactions of SSP, DAP, and PR.

A series of precipitation and adsorption reactions explains P behavior in soil (Barrow, 1983; Barrow, 1989; Holford, 1989). Precipitation–dissolution reactions dominate when there is a large change in the P concentration, when cation concentrations are high, and when soil pH is low or high, for example, in the immediate vicinity of a fertilizer granule (Hedley and McLaughlin, 2005). Adsorption–desorption processes dominate when P concentration changes are small, solution cation concentrations are low, and where micro-surfaces are large, such as in clay soils.

Even in quite dry conditions, water-soluble granular fertilizers absorb water on application to soil (Lawton and Vomocil, 1954). Surface-applied SSP is initially wetted directly from rainfall or irrigation, by capillary uptake of water, and by vapor transfer from the soil or atmosphere due to the hygroscopic nature of the MCP (Williams, 1969). Similar processes would be expected to occur for DAP except that the absence of the calcium sulfate carrier present in SSP would restrict the opportunities for capillarity. The high solubility of DAP would tend to enhance mass flow of soil water to the DAP granule once the wetting process has commenced by establishing a high osmotic gradient in the soil.

Factors affecting the ingress of water vapor into water-soluble fertilizer granules include relative humidity, temperature, and physical properties of the particles themselves such as size, shape, and porosity, and surface oil coatings designed to improve handling (Lawton and Vomocil, 1954; Williams, 1971b). For hygroscopic uptake of water by SSP, a relative humidity >89% is generally considered necessary (Williams, 1969) and is exceeded in most field soils (Payne, 1988). Lawton and Vomocil (1954) showed that even at low soil water contents (e.g., 2–4% w/w), water uptake and movement of phosphate out of SSP granules occurs rapidly (i.e., within hours). Recently, a method to visualize P dissolution and diffusion from fertilizer granules in situ (i.e., in soil) was developed that confirmed that the reaction is fast and virtually complete within 24 h (Degryse and McLaughlin, 2014).

Coatings applied to water-soluble fertilizer granules affect moisture uptake and P dissolution. For example, sulfur coatings have been used to slow the release of orthophosphate, thereby increasing P efficiency, and to address other nutrient deficiencies (Engelstad and Terman, 1980). Polymer coatings have also been used in developing controlled release fertilizers (da Cruz et al., 2017; Lambie, 1987; Shaviv and Mikkelsen, 1993; Umesha et al., 2017). Dust suppressants (e.g., oils and waxes) added to fertilizers during manufacture and transport would also be expected to slow water ingress and P egress from granules, but their effects appear to be small (University of Adelaide Fertilizer Technology Research Centre, unpublished data, 2018).

Monocalcium phosphate is the primary P component of superphosphate. As water is absorbed, the solution that forms within a superphosphate granule is supersaturated (Williams, 1971a), leading to the precipitation of sparingly soluble di-calcium phosphate dihydrate. Depending on the calcium activity, competing reactions (Bouldin et al., 1960), and complexation of inorganic ions, 20 to 34% of the TP may be precipitated as di-calcium phosphate dihydrate at the granule site (Lehr et al., 1959). Once dissolution is initiated, the highly acidic solution (pH 1.5) diffusing from superphosphate granules dissolves soil minerals, creating a concentrated solution of phosphate, calcium, sulfate, iron, aluminum, and other ions (Lindsay et al., 1959; Lindsay and Stephenson, 1959a, 1959b). As the process continues, vapor transfer and mass flow of water extend the wetted zone and a series of precipitation and adsorption reactions decrease the soil water P concentration (Fig. 1). The importance of these individual reactions depends on, among other things, the pH and relative proportions (i.e., activities) of the cations in the soil (Bell and Black, 1970a, 1970b; Engelstad and Hellums, 1992; Sample et al., 1980). In higher pH soils or those rich in calcium, initial dissolution and diffusion of P from SSP (or TSP) granules is retarded due to greater precipitation of di-calcium phosphate dihydrate in and around the granule (Degryse and McLaughlin, 2014; FTRC, 2019; Lombi et al., 2004).

The retention of ammonium phosphates in the soil is likely to be affected by the solution pH of these compounds, 3.5 for MAP and 8.0 for DAP (Lindsay et al., 1962). When applied to soil, MAP forms reaction products that are initially like those of MCP, di-calcium phosphate dihydrate unless exchangeable magnesium is high. In contrast, DAP forms a range of calcium and magnesium compounds such as calcium di-ammonium diphosphate monohydrate [$Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$], octacalcium hexaphosphate pentahydrate [$Ca_8H_2(PO_4)_6 \cdot 5H_2O$], calcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$), and magnesium ammonium phosphate hexahydrate ($Mg\ NH_4PO_4 \cdot 6H_2O$) (Bell and Black, 1970a; Moody et al., 1995). Interestingly, while DAP has been shown to increase soil pH near a granule application site, it decreased soil pH at the wetting front. In this zone, the acidity, that was attributed to the hydrolysis of water and the precipitation

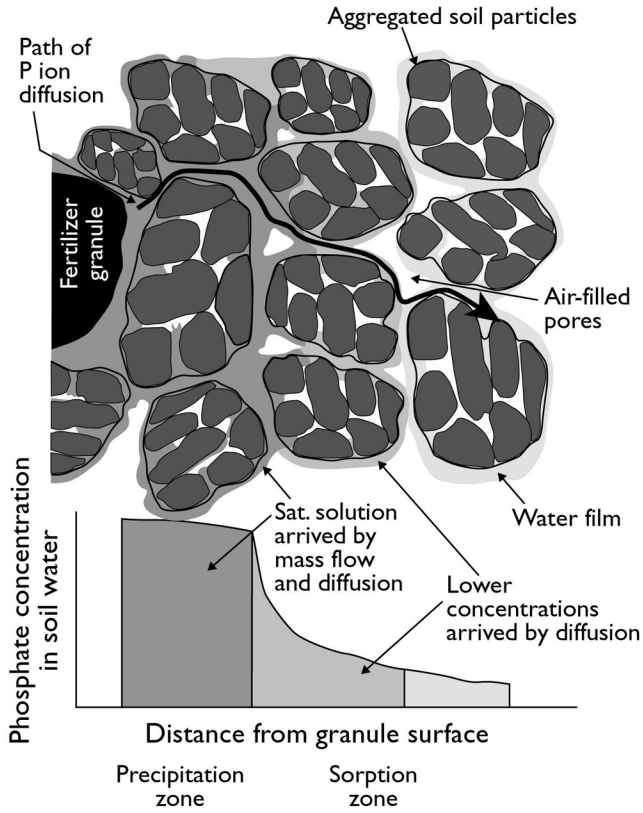

Fig. 1. A diagram representing the movement of phosphate out of fertilizer granules and into soils. Adapted from Hedley and McLaughlin (2005).

of more acidic compounds than DAP, such as MAP, appeared to dissolve soil components resulting in the precipitation of aluminum phosphates (Sample et al., 1979). Other studies have shown precipitation reactions involving calcium and magnesium can be important (Lombi et al., 2006; Moody et al., 1995). It is noteworthy that nitrification of ammonium from DAP is also likely to lower soil pH and affect P reactions in the longer term.

Finely ground reactive PR is primarily used as a fertilizer on acidic soils (Bolan and Hedley, 1997; Hedley and McLaughlin, 2005; Sale et al., 1997a, 1997b). Being sparingly soluble in soil water (equilibrium concentrations <0.030 mg P L^{-1} at pH 6), the overall availability of the P from PR depends on its rate of addition, surface area, mineralogy and chemical reactivity, and the ability of the soil–plant system to enhance dissolution and modify soil pH (Chien et al., 2011; Hedley and McLaughlin, 2005).

The low water solubility of PR lends itself to use in areas with considerable subsurface drainage and poor soil P sorption, such as Western Australia, where more water soluble fertilizers would not be retained in the root zone. However, a lack of quality rock and poor agronomic effectiveness (Simpson et al., 1997) in areas where the soil pH is ≥6 and rainfall is <800 mm has limited market penetration in Australia. Similarly, use of PR for direct application is a small proportion (4%) of the New Zealand market (McDowell et al., 2019). Less water soluble superphosphates (e.g., the SuperSR range of products from CSBP Fertilizers and lime-reverted SSP in New Zealand, often termed *dicalcic phosphates*), which are basically di-calcium phosphate dihydrate formed by treatment of SSP with lime, are sometimes used, but the agronomic efficiency of these products is usually greater than SSP only in situations where P leaching is significant (i.e., course-textured soils in high-rainfall environments) (Edmeades, 2000). Polymer-coated products, while effective in slowing P release from water-soluble products, are generally too expensive for widespread use on pastures and tend to be used more in horticultural production systems on light-textured soils, focused mostly on decreasing losses of nitrogen (Morgan et al., 2009).

Phosphorus Export Pathways in Agricultural Systems

Waterborne P exits field soils though several interrelated pathways (Fig. 2) that can be difficult to distinguish.

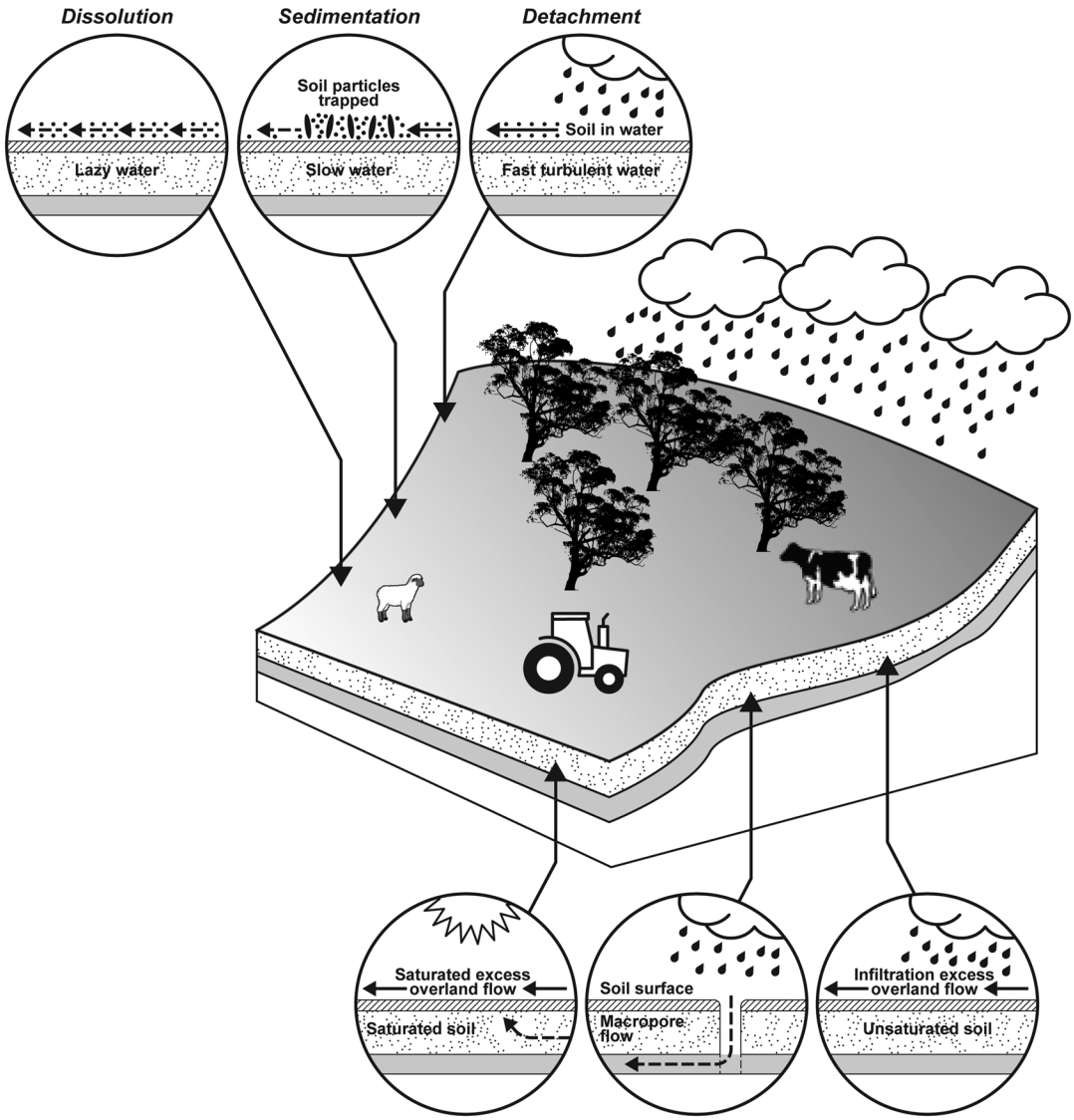

Fig. 2. Hydrology and P mobilization processes at the field scale. Adapted from Nash et al. (2002).

Infiltration-excess overland flow occurs where water additions exceed vertical drainage (i.e., the infiltration rate and the combined hydraulic conductivity of underlying layers is exceeded) (Emmett, 1978). Infiltration-excess overland flow is affected by factors that alter infiltration behavior such as hydrophobicity, slaking and dispersion, and soil compaction and structural deterioration that affect hydraulic conductivity (Cresswell et al., 1992; Hillel, 1980). Infiltration-excess overland flow tends to increase down slopes as run-on from higher areas increases the hydraulic load, and hence increase the probability of overland flow in receiving areas.

Saturation-excess overland flow is characterized by saturation of the subsoil. Infiltration may be occurring, but at a negligible rate due to the low hydraulic conductivity of the underlying strata. Soils with a permeable A horizon overlying a heavy clay, less-permeable B horizon (Chittleborough, 1992) are prone to such conditions (Cox et al., 2002; Cox and McFarlane, 1995). Saturation-excess overland flow also occurs where groundwater or interflow rises to the surface in discharge zones, often at the break of slope (Gerits et al., 1990; Moore and Foster, 1990; Rulon et al., 1985).

Once entrained, there are limited opportunities for amelioration of P transported through surface pathways. Sedimentation (Fig. 2) may remove some larger, more dense solids from overland flow, increasing the P concentration (Sharpley, 1980, 1985). However, solution or colloidal P (i.e., <0.45 μm), collectively termed *dissolved* P, are unlikely to be affected by such a physical process, and dissolved P concentrations in overland flow tend to increase with path length (and residence time) (Barlow, 2003; Doody et al., 2006; Nash and Barlow, 2009; Nash et al., 2007).

Matrix flow describes water moving vertically through the soil fabric (Nash and Halliwell, 1999). Matrix flow facilitates adsorption of orthophosphate and deposition of particulate P (i.e., >0.45 μm) depending on soil attributes (e.g., soil structure, P buffering capacity) and the intimacy (i.e., proximity and time) of the drainage and soil contact. Where water drains through stable macropores (e.g., fissures or biopores), P, especially dissolved P, can effectively bypass the soil matrix (Steenhuis et al., 1990).

Interflow describes water moving vertically into the soil without reaching groundwater and then laterally. Interflow can occur at the interface of the A/B or B/C horizons or in the A horizon, especially if a compacted layer has formed due to animal traffic. Interflow in the A horizon is difficult to functionally separate from overland flow. Consequently, the latter term will be used to describe them collectively. Like overland flow, interflow accumulates down a slope and, when the incident water and interflow exceed the soil transport capacity (i.e., hydraulic conductivity × soil thickness), overland flow is likely (Amerman, 1965).

The relative contributions of surface (e.g., overland flow) and subsurface pathways (e.g., interflow) to P exports have been studied at a range of scales (Green and Wang, 2008). Subsurface pathways are favored where substantial macroporosity exists in the subsoil clays (Cox et al., 2000) or water passes through poorly buffered soil (e.g., sand) (Mansell et al., 1977; Ozanne et al., 1961). Subsurface (e.g., tile) drains are the ultimate horizontal macropore facilitating interflow (Gächter et al., 1998; King et al., 2015; Kleinman et al., 2015; Monaghan et al., 2002). In the absence of significant macropore flow, overland flow appears to be the most important pathway for P exported from well-managed grazing systems in Australia and New Zealand, although evidence exists to show intensive land use has enriched New Zealand groundwater and baseflow P concentrations of some streams (McDowell et al., 2015).

Forms of Phosphorus in Agricultural Drainage and Their Mobilization into Water

Phosphorus is exported in pasture drainage either as part of a solid, attached to a solid, or as a solute (i.e., dissolved in water). The terms *dissolved* and *particulate* are commonly used to define P materials that pass through or are retained by a 0.45-μm filter (i.e., about the size of a virus or smaller). It follows that dissolved P may include some P attached to, or contained in, colloidal materials (Beckett and Hart, 1993; Haygarth and Sharpley, 2000). Phosphorus forms are further differentiated by their reactivity in an acid-molybdate solution where color formation relies on the presence of orthophosphate (Murphy and Riley, 1962). Due to the hydrolysis of acid-labile P compounds, the test may overestimate orthophosphate concentrations (Broberg and Pettersson, 1988; Burton, 1973; Halliwell et al., 2000a). The most commonly reported forms of P exported from pastures are TP, total dissolved P (TDP), and dissolved reactive P (DRP).

Phosphorus forms influence the effectiveness of mitigation strategies. For example, vegetative filter strips, commonly termed *buffer strips* (Hairsine, 1996; Hairsine and Grayson, 1993), use sedimentation to remove particulate P from overland flow but are less effective removing dissolved (i.e., TDP or DRP) forms (Dillaha et al., 1988; Grayson et al., 1994). A well-managed pasture field could itself be considered a "buffer" strip and, in the event of overland flow, be expected to yield predominantly dissolved forms of P (Nash and Murdoch, 1997; Sharpley et al., 1994)

The form in which P is mobilized also influences its impact on receiving waters. Particulate P (i.e., >0.45 μm) comprises crystalline P, adsorbed P, and P in organic matter that require transformation to orthophosphate before they are available to aquatic plants. On the other hand, orthophosphate is often a major component of dissolved P (i.e., <0.45 μm) and is immediately bio-available (Robinson et al., 1994; Walton and Lee, 1972). The potency of P exported in a dissolved form as compared to a particulate form is reflected in water quality guidelines that focus on dissolved P forms in flowing streams and rivers but TP in slow flowing large rivers and lakes and reservoirs (ANZECC and ARMCANZ, 2018; McDowell et al., 2013a, 2013b; Wilcock et al., 2007).

The mobilization of particulate P (i.e., solids) is primarily a physical process that commences with detachment of fine particles (sediments) and associated P from aggregates and other soil materials. The term *erosion* is commonly used to refer to a process whereby mobilization (i.e., detachment) is followed by entrainment of particulate materials in flowing water. Detachment is facilitated by physical processes including raindrop impact, cultivation, cattle treading damage, and flowing water and by physicochemical processes such as slaking and dispersion (Davies and Payne, 1988; Leeper and Uren, 1997). The capacity of water to transport particulate materials is related to the kinetic energy of

the water (Shainberg et al., 1994). Factors that increase water velocity (e.g., slope) and turbulence (e.g., obstructions) generally increase detachment and transport rates. Erosion processes are well reviewed elsewhere (Kelley, 1983; Smith and Wischmeier, 1962; Wischmeier and Smith, 1978).

The processes controlling mobilization of dissolved P are more complex, having both physical and chemical components. Factors that might be expected to affect dissolved P mobilization include the availability of soluble P sources, the sorption characteristics of the soil matrix in the immediate vicinity of P sources, the presence or absence of chelating agents or substances that may block adsorption sites (Guppy et al., 2005a, 2005b), and "residence time," the time available for soil and water interaction (Pierzynski et al., 2005). However, the strongest evidence regarding the nature of dissolved P mobilization comes from field-scale observations.

When rain falls, or irrigation water is applied to a pasture-based grazing system, it washes over and through vegetation and onto the soil surface. It is on the soil surface that animals defecate, fertilizers are often applied, and detritus from pasture plants and supplementary feed falls. It is also here, in the spongy mixture of inorganic and organic materials at the surface, that P mobilization is initiated. It follows that live plants and their detritus can be important sources of P (Sharpley, 1981; Toor et al., 2003). Relationships between the tannin color, dissolved organic carbon, and TDP in overland flow tentatively support that proposition (Halliwell et al., 2000b; Nash et al., 2014), as do studies measuring P, often orthophosphate, extracted from "hayed-off" *Phalaris*, clover (*Trifolium* spp.), and other plants (Bromfield and Jones, 1972; Jones and Bromfield, 1969; Noack et al., 2012).

Mixing layer models have been used to describe contaminant mobilization (Shi et al., 2011). They are particularly useful for conceptualizing mobilization of contaminants into overland flow. These models often comprise (i) a mixing layer near the surface from which materials (e.g., P) are rapidly mobilized (Process 1) and (ii) a slower mobilization process dominated by diffusion and hydraulic dispersion (i.e., mechanical mixing by velocity variations at the microscopic level during advective transport) that transfers materials into the mixing layer from below and facilitates P egress from aggregates or detrital material in the mixing layer (Process 2). The depth to which soil and water mix is a critical parameter as it determines the quantity of P available for rapid mobilization.

Tracer studies using simulated rainfall (68 mm h^{-1}) and repacked bare soil in boxes suggest the "effective depth of interaction," a composite of the mixing depth and soil supplying P into that region from below, can be <20 mm (Ahuja and Lehman, 1983), with extraction efficiency declining exponentially with depth (Snyder and Woolhiser, 1985). In similarly conducted model studies using ^{32}P, the mixing layer (i.e., the layer where the mobilization of P was consistent with that of the soil surface) for simulated rainfall (65 mm h^{-1}) was <3 mm (Ahuja et al., 1981).

If the depth of the mixing layer relates to rapid mobilization, then a mixing layer of ~3 mm might be expected for P in many well-managed pastures. Natural rainfall is often less intense than that used in simulation studies, and the pasture canopy and detrital material would be expected to intercept raindrops, lowering the kinetic energy available for aggregate disruption and mixing. On the other hand, surface perturbations from animal traffic may well increase the "apparent" (i.e., effective) depth of interaction by increasing the soil surface area and decreasing soil stability (Drewry, 2006; Drewry et al., 2008; Greenwood and McKenzie, 2001).

Field-scale processes that are difficult to simulate are also likely to affect the resupply of P into the mixing layer (Process 2). Infiltrating water can transport P away from the mixing layer, while return flow may do the opposite (Fig. 3). Depending on the field-scale hydrology, these may negate or overwhelm the effects of diffusion and hydraulic dispersion. It follows that resupply of P into the mixing layer can be influenced by soil water content, pore-size distribution and most important, soil infiltration characteristics (Ahuja, 1990; Kleinman et al., 2006; Snyder and Woolhiser, 1985; Vadas et al., 2008).

A mixing layer model is consistent with increasing wetting front TDP with path length in border-check (also called border-dyke) irrigation bays noted previously (Nash et al., 2007) and flume studies (Barlow, 2003; Doody et al., 2006). In border-check irrigation, high initial infiltration rates occur at the comparatively dry wetting front. But behind the wetting front, infiltration rates rapidly decline and overland flow increases (Nash and Barlow, 2009). Water samples, which by necessity are recovered from just behind the true wetting front, most probably have P concentrations that reflect initial P mobilization from the mixing layer and therefore increase with distance down the bay. In flume studies, and in the absence of infiltration, increasing P concentrations with time are likely to reflect P transported into the mixing layer by diffusion and hydraulic dispersion.

A mixing model also helps explain relationships between P concentrations and stormflow. Poor relationships are often observed between overland flow volume and flow-weighted P concentrations for individual storms (Nash et al., 2000, 2005; Owens and Shipitalo, 2006). Mobilization of P from the mixing layer (Process 1) early in a storm would be expected to rapidly give way to slower mobilization (Process 2) as the storm progresses. It follows that between-storm variation in flow-weighted P concentrations would more reflect event duration than total

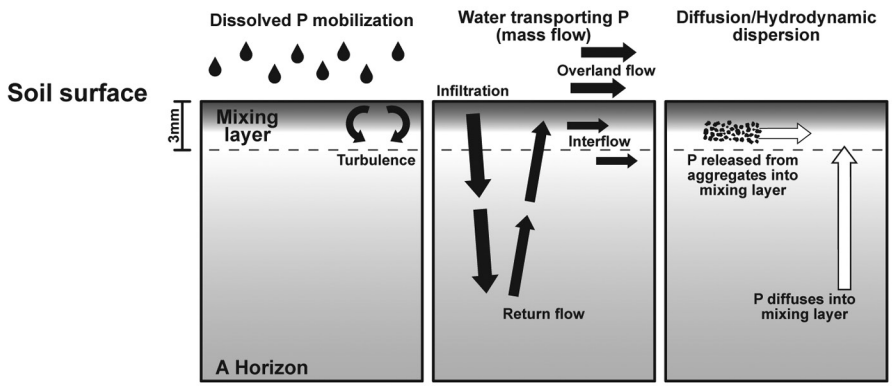

Fig. 3. Field-scale processes contributing to dissolved P mobilization.

flow volume. It also follows that within-storm P concentrations would tend to be inversely proportional to flow rate due to dilution. These attributes were exemplified in a study of rainfall-induced overland flow at Darnum in southeastern Australia comprising 61 storms over 7 yr (1994–2000). Flow-weighted TP concentrations for individual runoff events were unrelated to the flow volume (Nash et al., 2005). However, in many instances within-storm TP concentrations were related to the overland flow rate at the time (Fig. 4) (Nash and Murdoch, 1997). At that site, TDP comprised 93% of TP. Such studies emphasize the importance of time-dependent processes to field-scale P exports.

Quantifying the Short-term Impacts of Fertilizer on Phosphorus Exports

Numerous authors have investigated the effects of fertilizer application on P exports (Hart et al., 2004). Some such studies are summarized in Table 2. Rarely have these studies generalized the within-year (i.e., between-storm) variation associated with specific activities, such as fertilizer application, or the long-term trends in background (i.e., base or systematic) P exports. Most of these studies have demonstrated that it is possible for recently applied fertilizer to overwhelm other P sources. However, from a catchment management perspective the key question is not what is "possible," but rather what is "probable."

A conceptual model with background and management components has been used to investigate the effects of surface-applied fertilizer on a grazed pasture (1.8 ha) at Darnum in the Gippsland region of southeastern Australia (Eq. [1]) (Nash et al., 2000):

$$TP = k_i \times DAF^{-0.476} \times DAG^{-0.241} \times RUNOFF^{-0.105} \quad [1]$$

where TP is the flow-weighted mean total P concentration for the event (mg TP L^{-1}); DAF is the interval (d) between fertilizer application and overland flow; DAG is the interval (d) between grazing and overland flow; RUNOFF is the total overland flow volume (L) for the event; and k_i is a constant relating to year (i). While A/B-horizon interflow existed at the site, overland flow was primarily responsible for P exports with DRP being 93% of TP. A multiplicative model (Eq. [1]) using data from 34 storms over 3 yr explained 68% of the variance (adjusted R^2) in ln(flow-weighted TP). The interval between fertilizer application and overland flow was inversely related to TP ($P < 0.001$) and accounted for 50.6% (adjusted R^2) of the variance. The interval between grazing and overland flow, although significant, was less strongly correlated to TP. In keeping with a plot-scale study (Dougherty et al., 2008), the initial half-life of fertilizer impact (i.e., the number of days since fertilizing to decrease the TP concentration by half) was estimated to be 4.3 d, with 95% confidence interval of 3.1 to 8.0 d. There was no consistent effect of total storm flow on TP.

Equation [1] is empirical, developed to describe the data without necessarily reflecting the physical processes involved. While mathematically correct, it implies that the factors affecting flow-weighted P concentrations are inappropriately interrelated. For example, the effects of fertilizer application decay with time after grazing (e.g., if grazing occurs a long time before fertilizer application and subsequent overland flow, then the effects of fertilizer application are minimized)

In a similar study using broiler litter applied to pasture in the United States, a more conceptually sound, additive model was used. The model, which incorporated terms for background (i.e., base) and management components, explained 70% of the variance in DRP concentrations in overland flow (Pierson et al., 2001). Again, time between P application and overland flow was the most influential term in the model, explaining 32% of the total variation.

A similarly conceptually sound, additive model (Eq. [2]) was used to investigate 124 events (>2500 L), 61 from Darnum (1994–2000) and 63 from border-check (i.e., flood) irrigated pastures at the Macalister Research Farm (1999–2000) in central Gippsland (Nash et al., 2005):

$$TP_{ij} = \left(\text{Initial concentration of P in added water}\right) + \frac{(\text{P from grazing}) + (\text{P from fertilizer}) + (\text{Background P})}{\text{Volume}} \quad [2]$$

where TP is the TP concentration (mg TP L^{-1}) in overland flow for that event. It is noteworthy that in keeping with the processes leading to dissolved P mobilization presented earlier, there is assumed to be no interaction between fertilizer application and grazing. The relationship between overland flow volume and flow-weighted TP was again insignificant, as was the initial P concentration in added water. Concentrations in overland flow varied from 1.4 to 110.0 mg TP L^{-1} at Darnum and 1.6 to 103.5 mg TP L^{-1} at the Macalister Research Farm. The highest P concentrations occurred when fertilizer application and overland flow coincided.

The flow-weighted annual P concentrations varied between 3.3 and 28.2 mg TP L^{-1} for Darnum and 6.2 and 31.5 mg TP L^{-1} for the Macalister Research Farm. The models explained 61 and 70% of the variation in log-transformed TP for Darnum and the Macalister Research Farm, respectively, with the base and management factors all highly significant (Fig. 5). The fertilizer half-lives were slightly shorter than the previous Darnum study, 2.9 d (95% confidence interval 1.7–9.3 d) for Darnum and 3.9 d (95% confidence interval 2.8–6.1 d) for Macalister Research Farm. Even though soil fertility at the Darnum site

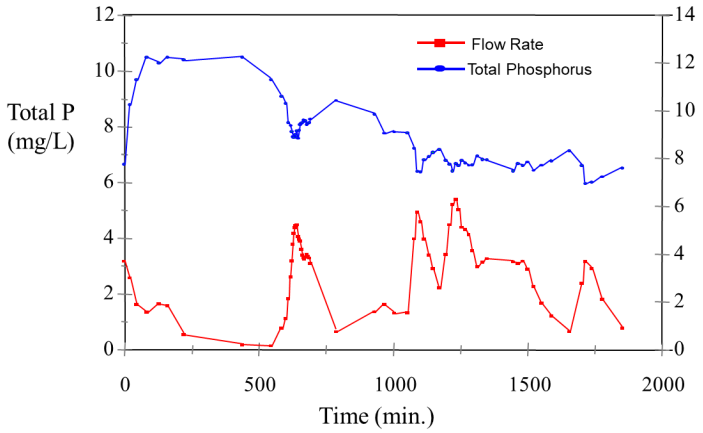

Fig. 4. Within-storm variation in total P concentration and flow from a field in the Darnum region of West Gippsland, Australia, on 6 Nov. 1994. Source: Nash and Murdoch (1997).

Table 2. Selected studies investigating the effects of inorganic fertilizer application on P exports from grassed systems.

Study location	Fertilizer type and application rate†	Study area (ha)	Experimental conditions	Phosphorus concentration range‡	Phosphorus export‡	Source
New Zealand	Various fertilizers and rates were applied	248 38 1.44	Natural rainfall, grassed hill country pasture with streamflow monitoring in nested design	0.003–0.051 mg TDP L^{-1} 0.007–0.20 mg TDP L^{-1} 0.026–1.49 mg TDP L^{-1} for respective catchments	–	McColl, 1978
New Zealand	SSP aerially applied at 30 kg P ha^{-1}	20	Natural rainfall on pasture with streamflow gauging	<0.5–1.56 mg TPP L^{-1} <0.05–9.83 mg DRP L^{-1}	0.6 kg DRP ha^{-1} 1.59 kg TP ha^{-1} attributed to fertilizer	Sharpley and Syers, 1979
New Zealand	SSP applied above collectors at ~50 kg P ha^{-1}	Within paddock samplers	Natural rainfall on hill country pasture with overland flow monitoring	1.2–1.46 mg TP L^{-1}, ungrazed 1.16–25.8 mg TP L^{-1} grazed	–	McColl and Gibson, 1979
USA	Ammonium phosphate applied at 75 kg P ha^{-1}	9.6 11 7.8 11.1	Natural rainfall on pasture in paired catchments	0.025–6.49 mg TDP L^{-1} 0.44–8.21 mg TP L^{-1}	3.3 kg TDP ha^{-1} 4.1 kg TP ha^{-1} attributed to fertilizer	Olness et al., 1980
New Zealand	SSP in liquid and solid forms applied at 50 kg P ha^{-1}	0.0055 0.0055 0.0041	Natural rainfall on permanent pasture plots measuring overland flow	0.2–4.1 mg DRP L^{-1} 0.3–4.3 mg TPP L^{-1}	1.4 kg DRP ha^{-1} and 2.9 kg TP attributed to solid SSP and 0.5 mg DRP ha^{-1} and 1.2 kg TP ha^{-1} to liquid SSP annually	Sharpley and Syers, 1983
Australia	SSP applied at 0, 100, 200, and 400 kg P ha^{-1}	0.004	Natural rainfall on permanent pasture plots measuring overland flow	0.7–62.9 mg DRP L^{-1} 1.0–66.9 mg TP L^{-1}	<0.1–0.40 kg DRP ha^{-1} <0.2–0.45 kg TP ha^{-1}	Greenhill et al., 1983a, 1983b, 1983c
New Zealand	Mainly superphosphate applied at 11 and 64 kg P ha^{-1}	0.13–1.53	Natural rainfall on hill country pasture measuring overland flow	–	0.66–1.95 kg TP ha^{-1} annually	Lambert et al., 1985
USA	Commercially available inorganic fertilizer blend surface applied or incorporated at 87 kg P ha^{-1}	0.0009	Simulated rainfall (50 mm h^{-1}, applied for 30 min after drainage commenced) with fescue pasture on non-incorporation treatments measuring overland flow	–	1.5 kg DRP ha^{-1} 1.7 kg TP ha^{-1}	Nichols et al., 1994
Australia	SSP applied at 0, 22, 44, 66, 88 kg P ha^{-1}	0.024	Border-check irrigation of white clover–ryegrass pastures measuring tailwater overland flow	~<0.5–119 mg DRP L^{-1} ~<0.5–121 mg TP L^{-1}	~7.7–15 kg TP ha^{-1}	Austin et al., 1996
UK	TSP applied at 16 kg P ha^{-1}	1	Natural rainfall on ryegrass pasture measuring overland flow to 300 mm soil depth	<0.02–1.30 mg DRP L^{-1} <0.03–1.77 mg TP L^{-1}	~3 kg TP ha^{-1} annually	Haygarth and Jarvis, 1997
UK	DAP applied at 150 kg P ha^{-1}	0.015	Simulated rainfall (22 mm h^{-1}) applied to hillslope ungrazed permanent pasture plots for 35 min on 4 consecutive days	15.3 mean mg TP L^{-1} for fertilized plots	~2.5 kg DRP ha^{-1} ~3.6 kg TP ha^{-1}	Heathwaite et al., 1998
UK	TSP applied at 29 kg P ha^{-1}	0.003	Natural rainfall (48.8 mm in 169 h with rain intensity ≤3 mm h^{-1}) on perennial ryegrass, cattle and sheep grazed pasture, causing 46 mm drainage measuring overland flow to ~300 mm	<0.10–11.0 mg TP L^{-1}	1.8 kg TP ha^{-1} of which ~70% was DRP during the 7-d experimental period	Preedy et al., 2001
Australia	SSP applied at 44 kg P ha^{-1}	0.024	Border-check irrigation of white clover–ryegrass pastures measuring tailwater overland flow	0.45 to ~89 mg DRP L^{-1} 0.35–98 mg TP L^{-1}	2.6–15 kg TP ha^{-1} over 3 irrigations	Bush and Austin, 2001
USA	Inorganic fertilizer assumed to have only soluble P applied at 25 and 50 kg P ha^{-1}	0.0006	Natural rainfall of common Bermudagrass measuring overland flow	1.1–30 mg DRP L^{-1}	~8.5 kg P ha^{-1} lost in 8 monitored runoff events and plant uptake	Gaudreau et al., 2002
New Zealand	SSP applied at ~17, 22, or 33 kg P ha^{-1} and reactive PR at 175 kg ha^{-1}	0.000021	Simulated rainfall (15 mm h^{-1} with samples taken for 1 h after flow started) on intact turfs of varying fertilizer history measuring overland flow	0.01–5.40 mg DRP L^{-1} 0.17–6.98 mg TP L^{-1}	–	McDowell et al., 2003

Table 2. Continued.

Study location	Fertilizer type and application rate†	Study area (ha)	Experimental conditions	Phosphorus concentration range‡	Phosphorus export‡	Source
USA	SSP applied a 0, 22, 66, and 110 kg P ha^{-1}	0.0004	Simulated rainfall (76 mm h^{-1} applied for 30 min after drainage commenced) on field plots	0.18 to ~5.5 mg DRP L^{-1} 1.60 to ~13 mg TP L^{-1}	0.03 to ~1.1 kg DRP ha^{-1} 0.26 to ~2.0 kg TP ha^{-1}	Tarkalson and Mikkelsen, 2004
Australia	SSP and DAP both surface-applied at 50 kg P ha^{-1}	~1.1	Border-check irrigation of white clover–ryegrass pastures measuring tailwater overland flow for the rainfall study and on-bay wetting front sampling for the irrigation study	Rainfall, SSP 63 mg TDP L^{-1}, 70 mg TP L^{-1}, DAP 89 mg TDP L^{-1}, 97 mg TP L^{-1}, Irrigation, mean SSP <23 mg TDP L^{-1}, DAP <15 mg TDP L^{-1}	Rainfall only, SSP 5.5 mg TP ha^{-1}, DAP 9.0 mg TP ha^{-1}	Nash et al., 2004
New Zealand	SSP, PastureZeal, serpentine super, Gafsa reactive phosphate applied at 30 kg P ha^{-1} (water soluble P in each fertilizer, 82.8, 56.7, 12, and 0.9 g kg^{-1})	0.000021	Simulated rainfall (17 mm h^{-1} with samples taken for 1 h after flow started) on intact turfs measuring overland flow	~0.01 to ~70 mg DRP L^{-1} ~0.05 to ~78 mg TP L^{-1}	–	McDowell and Catto, 2005
USA	North Carolina PR, low-grade SSP, TSP (water soluble P contents 0.6, 39.9, and 159 g kg^{-1}) applied at a rate of 100 kg TP ha^{-1}	0.0002	Simulated rainfall (50 mm h^{-1} for 30 min after runoff commenced) applied to field plots with orchardgrass and no-till corn	Orchardgrass and no-till corn treatments 0.27–90.47 mg DRP L^{-1} 0.34–98.06 mg TP L^{-1}	Orchardgrass only 0.23–32.16 kg DRP ha^{-1} 0.31–33.16 kg TP ha^{-1}	Shigaki et al., 2006
USA	TSP applied at a rate of 39 kg TP ha^{-1}	0.00015	Simulated rainfall (50 mm h^{-1} for 30 min after runoff commenced) applied to field plots with Bermudagrass pasture	<23 mg DRP L^{-1}	<3.22 kg DRP ha^{-1} <3.86 kg TP ha^{-1}	Franklin et al., 2006
USA	Mono-ammonium phosphate either incorporated or surface applied or sliced surface applied at a rate of 76 kg P ha^{-1})	0.0004	Simulated rainfall (50 mm h^{-1} for 20 min after runoff commenced) applied to field plots with Bermudagrass and mixed grass forage	<1 to ~17 mg DRP L^{-1} 0.56–21.91 mg TP L^{-1}	Over 2 simulations 0.058–1.45 kg DRP ha^{-1} 0.104–1.74 mg TP ha^{-1}	Pote et al., 2006
USA	North Carolina PR, low-grade SSP, TSP (water soluble P contents 0.6, 39.9 and 159 g kg^{-1}) applied at a rate of 100 kg TP ha^{-1}	0.00002	Simulated rainfall (25, 50, and 75 mm h^{-1} to achieve 25 mm application volume) applied to trays planted with ryegrass	0.10–32.07 mg DRP L^{-1} 0.16–34.39 mg TP L^{-1}	–	Shigaki et al., 2007
Australia	A mixture of single and TSP was applied at rates of 0, 20, 40, 80 kg P ha^{-1}	0.125	Natural rainfall and sprinkler irrigation (8 mm h^{-1} for 10 h) induced overland flow from ryegrass and white clover grazed pasture	DRP is 86% of TP 0.86–11.13 mg TP L^{-1}	0.16–1.11 kg TP ha^{-1} annually	Dougherty et al., 2008
New Zealand	Superphosphate or reactive PR applied at 20–25 kg P ha^{-1}	12	Natural rainfall on hill country pasture measuring streamflow	0.01–2.00 mg DRP L^{-1} 0.01–12.0 mg TP L^{-1}	0.11 kg DRP ha^{-1}, 0.36 kg TP ha^{-1} superphosphate 0.05 kg DRP ha^{-1}, 0.21 kg TP ha^{-1} reactive PR	McDowell et al., 2010

† DAP, di-ammonium phosphate; PR, phosphate rock; SSP, single superphosphate; TP, total P; TSP, triple superphosphate.

‡ DRP, dissolved reactive P; PR, phosphate rock; TDP, total dissolved P; TP, total P; TPP, total particulate P.

increased from 17 to 57 mg P kg^{-1} during the study, there appeared to be no relationship between soil test P and the base (i.e., background) P concentrations (Fig. 5d). The results of the Darnum and Macalister Research Farm studies are consistent with similar field-scale studies elsewhere (Owens and Shipitalo, 2006).

The additive models developed for Darnum and the Macalister Research Farm have been used, along with fertilizer distribution, grazing and regional overland flow data, to quantitatively estimate P exports attributable to recently applied fertilizer (Nash and Hannah, 2011). The resulting Monte-Carlo simulations and Bayesian Networks demonstrate that for systems like those for which the equations were derived, P exports directly attributable to fertilizer application (i.e., short-term effects of recently applied fertilizer) are unlikely to have a major impact (i.e., <10%) on annual P exports. Fertilizer application accounted for between 5 and 18% and between 4 and 17% of total P exports annually from Darnum and the Macalister Research Farm, respectively. In this study, it was assumed that fertilizer application and overland flow occurred at random within a given month. In many regions, conditions conducive to overland flow, such as high antecedent soil moisture, preclude fertilizer application. Moreover, as a result of extension activities, farmers are now less inclined to apply

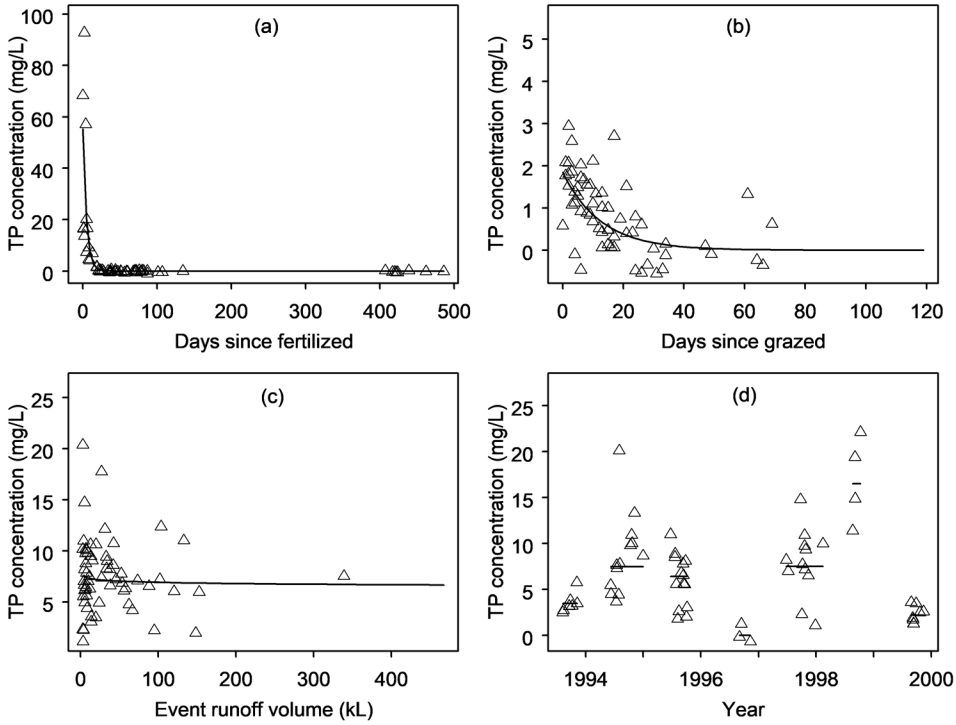

Fig. 5. Relationships between adjusted (partial residual) total P concentrations (TP) in overland flow and (a) days since fertilizer was applied, (b) days since last grazed, (c) overland flow volume for the event, and (d) the effect of year, for a site at Darnum in southeastern Australia. Points are back-transformed partial residuals (i.e., data with other model term estimates subtracted out). Lines are the relevant terms from the fitted model. Source: Nash et al. (2005).

fertilizer immediately before overland flow, inducing irrigation or rainfall (Department of Primary Industries, 2006). It follows that improved management of fertilizer application on a regional basis would of itself probably result in only a small (i.e., <10%) decline in total P exports.

Interestingly, in the Bayesian Networks discussed above, grazing appeared to make a bigger contribution to total P exports than fertilizer. While such findings need to be viewed with caution, they are plausible. Grazing increases water-available P in the mixing layer at the soil surface (McDowell et al., 2007; Mundy et al., 2003; Nexhip et al., 1997), and grazing occurs more often at times of the year when overland flow is more frequent (e.g., during the irrigation season and late winter and early spring in rainfed systems).

A New Zealand study (McDowell and Catto, 2005) used simulated rainfall on intact soil turfs (1050 mm long by 200 mm wide) to investigate the effects of different fertilizer formulations on P exports in overland flow 1, 7, 14, 28, 112, and 192 d after fertilizer application. Decay curves were used in conjunction with monthly overland flow data to show that the risk of direct fertilizer P exports was greatest in June when most overland flow occurs. The decay curves were then used with 2 yr of field monitoring data to simulate P exports from fertilizer applications occurring on 1 June and 1 December. From this semi-empirical approach, it was concluded that if applied in December, soluble P fertilizers would account for <10% of total P exports for the year (McDowell et al., 2009b; McDowell and Catto, 2005). While the methodology did not readily lend itself to detailed scenario testing and the outcomes of the study have been questioned (Quin et al., 2004), they are consistent with other modeling (Vadas et al., 2015).

Implications for Fertilizer Good Management Practices

Under good management practice where the principles of 4Rs are followed (Bruulsema, 2018; Johnston and Bruulsema, 2014), P exports attributable to recently applied fertilizer can be a relatively small proportion (i.e., <10%) of total P exports. However, particularly in New Zealand, where intensive pastoral agriculture has expanded into areas of increased risk for P exports (i.e., greater slope, poorer soil P sorption), the adverse consequences of inappropriate selection of the form, placement, rate, and timing of P fertilizer applications are increasing. For example, fertilizer selection is important in situations where there is regular and frequent rainfall (McDowell, 2010), poor soil P sorption (McDowell and Monaghan, 2015), high hydraulic fluxes (Simmonds et al., 2015), or soil properties (e.g., acid soil pH) that result in the rapid dissolution of calcium phosphates (Simmonds et al., 2016).

Due to the variability in farming systems, we use three model systems with varying hydrology to demonstrate the principles for selecting fertilizers to minimize P exports soon after their application (Fig. 6). Such systems are common to Australia and New Zealand, and while recognizing there are other options (Lombi et al., 2004; Lombi et al., 2005; Smith et al., 2016), discussion here is limited to the surface application of the mineral fertilizer compounds commonly used in pastoral systems.

Model System 1: Overland Flow–Dominated Hydrology

In overland flow–dominated systems (Fig. 6a) with seasonal rainfall, basal (i.e., annual) applications of P fertilizers should be undertaken when the probability of overland flow

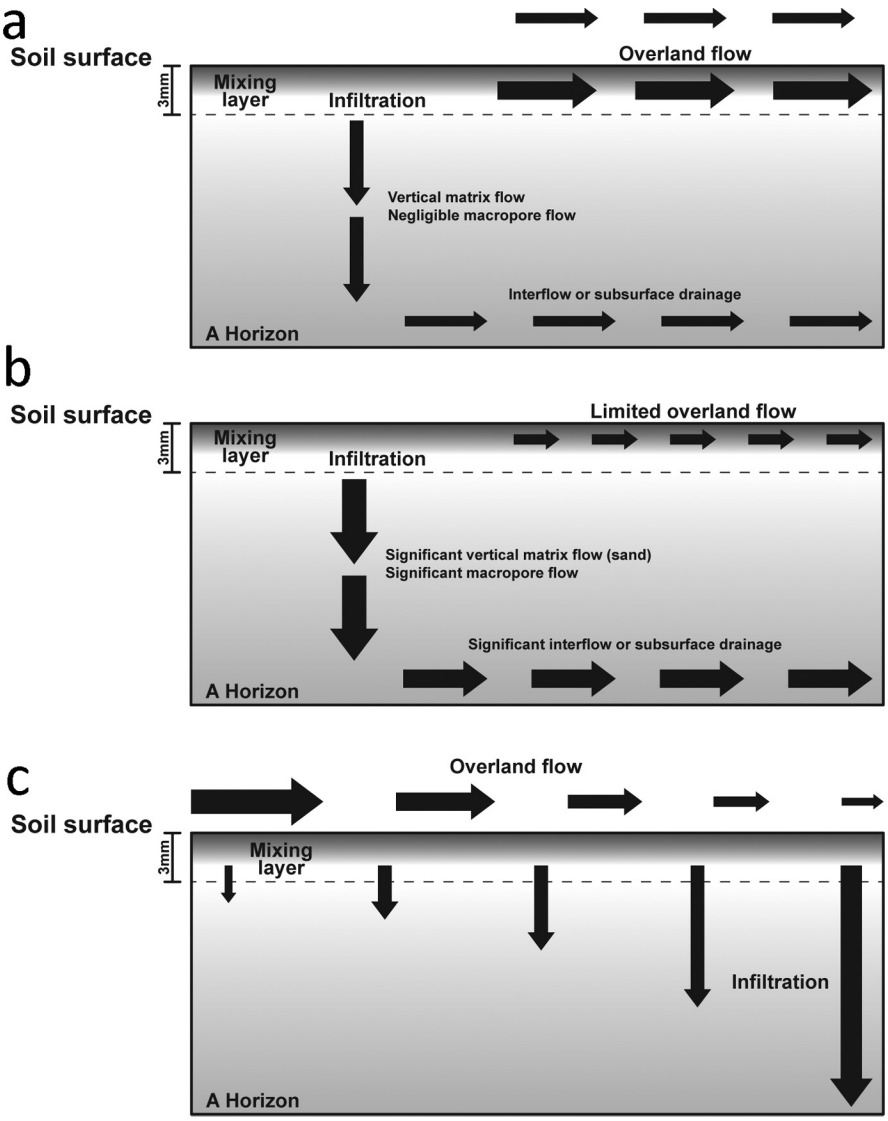

Fig. 6. Schematic representation of field-scale hydrology in selected farming systems: (a) overland flow dominant hydrology, (b) infiltration dominant hydrology including macropore flow to subsurface drains, and (c) border-check irrigation hydrology.

is lowest, for example, late autumn in southeastern Australia. Late autumn and early winter rainfall onto dry soil would be expected to transport dissolved P below the soil surface, lowering P concentrations in the mixing layer. Moreover, by maximizing the time between fertilizer application and overland flow, retention reactions should also minimize the P exports. Under those circumstances, fertilizer selection should be based on agronomic efficiency.

Fertilizer selection is likely to be more important where there is frequent (e.g., >50 overland flow events) and reliable (e.g., >4000 mm rainfall annually) year-round rainfall (McDowell, 2010), the soils are hydrophobic (Simmonds et al., 2017), or there are accidental additions of fertilizer-P to stream channels from aerial applications in steeper country (McDowell et al., 2010). In those instances, sparingly soluble or slow release fertilizer could well be the most appropriate, providing the agronomic objectives for its application are achieved. In a paired-catchment study (McDowell et al., 2010), application of reactive rock phosphate over 3 yr decreased DRP and TP loads in streamflow by 58 and 30%, respectively, compared with the same rate of P applied as superphosphate. However, there are many site-specific factors to consider.

In New Zealand, for example, the application of reactive PR has been shown to produce the same mass of pasture as TSP after 3 yr, provided there is sufficient rainfall (>800 mm) and the soil pH is <6 to allow the PR to dissolve (Sinclair et al., 1990). The lag in the performance of PR means that it cannot be used as a capital application of P to raise soil fertility quickly and must also be slowly introduced, increasing the proportion in the blend by a third each year.

While partially water-soluble fertilizers are probably the most appropriate form of P for applications in periods when overland flow is likely, that may not always be the case. For example, in southeastern Australia, formulations containing P (sometimes referred to as booster products) are used to stimulate short-term pasture production in early spring. If applications can be timed to avoid overland flow in the next 7 d or more (McDowell and Catto, 2005; Nash et al., 2004), P exports from water-soluble P in booster products should be relatively minor. In that case, the required root-zone P concentration could be achieved at a lower total P application rate than if partially water-soluble forms of P had been used. It follows that when managed appropriately and consistently, water-soluble P in booster products can help minimize the legacy effects (i.e., background exports) associated with increasing residual P in the soil–plant system. This is particularly true for very intensive systems where cattle traffic may enhance particulate P exports, which might include fertilizer solids, during vulnerable times of the year.

Model System 2: Subsurface Flow–Dominated Hydrology

In subsurface flow–dominated systems (Fig. 6b), the potential for P exports depends the ability of the soil to remove P in transit. Where macropore flow dominates, surface applications of P can result in significant P exports if drainage occurs soon after application. This is especially true where artificial drainage systems intercept vertical macropore flow and convey it to waterways (Monaghan et al., 2016). Erosion of macropores and drains from frequent flows can exacerbate P exports from these systems (Addiscott and Thomas, 2000).

As in systems where overland flow dominates, the timing of fertilizer application in relation to drainage is important in determining the most appropriate fertilizer formulation. Fertilizer

formulation is of lesser but not negligible importance where application and macropore drainage are unlikely to coincide. Less-soluble fertilizers may well be appropriate where they are applied to wet or dry cracked soils (Williams et al., 2003, 2016). Fertilizer P could be applied during pasture renewal where cultivation destroys macropores in the topsoil. However, the long-term effectiveness of this strategy is questionable given that macropore flow is often restored by earthworm activity within a year of cultivation (Dodd et al., 2014), pasture renovation is not usually an annual event, and cultivation may simultaneously increase erosion and particulate P exports in overland flow (Williams et al., 2016).

In systems where matrix flow predominates, P exports are largely determined by the P sorption capacity of the soil. For example, in New Zealand, subsurface drainage from runoff plots with varying anion storage capacity (ASC) (i.e., P sorption potential) were compared (McDowell and Monaghan, 2015). Over an 18-mo period, drainage from the plots was similar across all three sites (521–574 mm). Exports from a Podzol (55% anion storage capacity) that had been developed into pasture for 10 yr was 1.7 kg TDP ha^{-1}. However, the export of TDP leached to 35-cm depth from an organic soil was 87 kg P ha^{-1} (~89% of fertilizer-P added).

Mitigation measures tested in a New Zealand study included reduced P applications, applying alum (50 kg Al ha^{-1}) to improve the P sorption and applying low water-soluble reactive PR (McDowell, 2015). Alum reduced exports by approximately one-third, but that effect was likely to be transient as alum would be quickly leached from the soil or converted into more crystalline and unreactive forms. The application of PR was marginally effective but did not lessen P exports when pH was <5.5 (Simmonds et al., 2016). Hence, it was concluded that P application rates should be decreased and the intensity of the system lowered.

In Western Australian, studies using sandy pasture soils, P in leachate from SSP and coastal superphosphate (equal parts SSP, PR, and sulfur) were compared. Phosphorus was released quicker from SSP than coastal superphosphate and increased P exports by 10 to 40%. However, in the long-term, non-water-soluble components of fertilizer contributed to P in leachate, emphasizing the need to consider the legacy effects of fertilizer P (Weaver et al., 1988a, 1988b).

Subsurface pathways can also dominate the hydrology of irrigated pasture systems. Under spray irrigation, the potential for overland flow should be minimal, but substantial P exports can occur via subsurface flow, especially if the soil has a poor capacity to adsorb P or irrigation practice is poor. In a study in Central Otago, New Zealand, P exported in subsurface drainage was measured for 3 yr under a uniform rate irrigation from a sandy-textured soil (anion storage capacity <20%) (McDowell, 2017). Exports decreased by 70% following soil mapping and the recalibration of water application rates to match soil types beneath the irrigator. This example clearly shows the benefits of considering hydrology in combination with the 4Rs of nutrient stewardship, and the site-specific nature of P exports through subsurface pathways. While a wide range of factors bears consideration in selecting an appropriate fertilizer, where agronomically viable alternatives are available, water-soluble fertilizers are probably inappropriate for many systems with significant subsurface drainage (e.g., macropore flow, poor soil P sorption).

Model System 3: Border-Check Irrigation

Border-check irrigation, which is used to supplement natural rainfall, has a consistent pattern of hydrology (Fig. 6c). While gradually being changed to spray irrigation, border-check irrigation was once common in both Australia and New Zealand. Border-check irrigation is characterized by high infiltration rates at the wetting front. Here water traverses dry soil but infiltration rates decline rapidly behind the wetting front, back up the bay toward the water inlet. Tailwater (e.g., overland flow) from behind the wetting front enters drains at the foot of the bay, carrying with it predominantly dissolved P.

In border-check irrigation systems, land managers control water inflow and outflows to and from their bays. It follows that the best way of lessening P exports from P fertilizer applied during the irrigation season is short watering (i.e., minimizing drainage by not watering the final portion of the bay) and/or recycling tailwaters. However, some drainage (i.e., tailwater) from bays and farms is inevitable.

It is tempting to think that sparingly soluble or slow release fertilizers will minimize P exports from border-check irrigation. This is probably true if fertilizers are applied and irrigation occurs a week or two later. However, if high-risk periods are avoided, New Zealand studies have shown that for soils receiving long-term applications of reactive PR, P exports in tailwater >60 d after application can be greater than from soils receiving the same (i.e., long-term) rate of P applied as SSP. As a result, annual P exports may be higher from reactive PR as compared to water-soluble P fertilizer (McDowell et al., 2003).

Water solubility is not the only factor to consider in selecting the most appropriate fertilizer for border-check irrigation systems. An Australian laboratory study examined the mobilization of P from individual fertilizer granules and showed that when applied to acidic soil, P was released more rapidly from DAP than SSP (Nash et al., 2003). That result was consistent with subsequent field trials where P concentrations in flow sampled immediately behind the true wetting front were lower for DAP than SSP. It was postulated that compared with SSP, P was rapidly released from DAP and infiltrated at the wetting front during irrigation, lowering the P concentration in the mixing layer and the quantity of P subsequently available for mobilization (Nash et al., 2004). In that study, rainfall on recently irrigated pastures yielded the opposite result. That finding was attributed to a lack of infiltration (i.e., mass flow of P below the mixing layer) and the P from DAP being released more quickly into the mixing layer and mobilized in the wetting front. A more rapid release of P from ammoniated phosphates than SSP has been observed in other studies (Degryse et al., 2013). Especially in alkaline soils with high exchangeable calcium, SSP dissolution is delayed and diffusion from the granule initially limited by a common ion effect. Such studies suggest that there will be soil-specific differences in the relative benefits of compounds within solubility classes (i.e., SSP and DAP).

Concluding Comments

There is little doubt that not following the 4R principles for P fertilizers can result in excessive P exports from grazing systems in Australasia. This paper has focused on the short-term effects of fertilizer application on P exports and the selection of

appropriate compounds and formulations to minimize the associated risk to downstream water resources. Numerous studies have shown what is possible soon after fertilizers are applied. But the important question is not "What is possible?" but "What is probable?"

Using conceptually sound empirical models, it is possible to investigate the likely contribution of recently applied fertilizer to overall P exports from these systems. These analyses suggest that with good management practice, recently applied fertilizers make a minor (e.g., <10%) contribution to total P exports. But that is not necessarily the case where, for example, the soil has a poor sorption capacity, there is frequent rainfall, or fertilizer applications coincide with drainage events. However, by understanding the processes responsible for P mobilization, and the pathways through which P may be exported, it should be possible to mitigate the short-term risks associated with fertilizer use through prudent selection of compounds and formulations, and optimizing their application in terms of rate, timing and placement (i.e., applying the 4R concept).

Fertilizer good management practices are cost effective compared with other mitigation strategies that occur at the edge of the field or in-stream (McDowell and Nash, 2012). Their catchment-scale efficacy and cost-effectiveness in mitigating P exports is improved if they are targeted at critical source areas (i.e., areas within a farm or farms within a catchment) where surface and/or subsurface drainage are prevalent. For example, when appropriate P mitigation strategies were applied to 14 catchments in New Zealand, P exports were estimated to be halved with minimal impact on farm profitability (<2% of farm earnings before interest and tax) (McDowell, 2014). In New Zealand, semiquantitative evidence suggests that despite intensive land use expanding, good management practice combined with increasing awareness of P and critical source areas, and their reinforcement through voluntary processes and regulation, has seen stream water P concentrations decrease in the last 10 years (McDowell et al., 2019).

Conflict of Interest

The authors declare no conflict of interest.

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